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Control of Surface Properties Using Fluorinated Polymer Brushes Produced by Surface-Initiated Controlled Radical Polymerization

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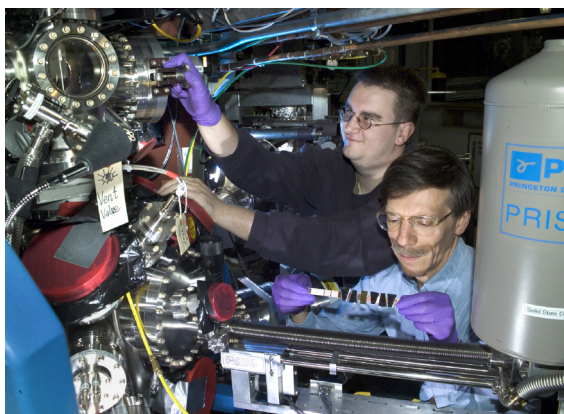
*Fluorinated polymers possess the important technological property of having very low surface energy. One familiar fluoropolymer is Teflon. When a surface prepared using a polymer that contains a fluorinated component is thermally annealed above its glass transition temperature, the low-energy fluorinated component will migrate to the air-coating interface. We are interested in fluorinated block copolymers for the creation of environmentally friendly, fouling-resistant coatings for marine applications. Anyone who owns a boat will know that it can quickly foul, that is, its hull can become coated with a biofilm created by marine flora and fauna. Fluoropolymers may permit the easy removal of foulants without the need for the toxic materials presently used in marine coatings. In a prime candidate for such a coating, surface segregation of a fluorinated block in a block copolymer can be effectively studied by near-edge x-ray absorption fine structure (NEXAFS) and detected by the presence of a sharp peak at 292.0 eV due to the $C\ 1s \rightarrow \sigma^*_{C-F}$ transition in the spectrum of Auger electron yield versus energy of the incident X-ray photon. In collaboration with researchers from the National Institute of Standards and Technology (NIST), NEXAFS studies are proving vital in understanding the surface properties of fluoropolymers.*

Grafting a fluoropolymer to a surface seems like an ideal way to coat a substrate with a low-energy polymer. When a block copolymer containing a polystyrene block and a fluorinated block has the free end of the polystyrene block tethered to a substrate, and is then annealed under vacuum, there are surprising results. The mobility of the fluorinated block is so restricted due to chemical bonding with the surface that the air-polymer interface is populated with the higher surface-energy polystyrene block. These were some of the important findings in the paper by Andruzzi et al. [L. Andruzzi, A. Hexemer, X. Li, C.K. Ober, E. J. Kramer, G. Galli, E. Chiellini, D.A. Fisher, *Langmuir*, **2004**, 20: 10498-10506]. Andruzzi and coworkers prepared fluorinated block copolymer brushes using surface-initiated controlled free radical polymerization. The polymerization reactions

were set into motion by initiator molecules covalently bound to a silicon substrate. The thicknesses of the brushes were found to be greater than the radius of gyration of the block copolymer molecules. This indicated that the tethered polymer chains were densely packed on the surface and were in a stretched configuration. The dense packing was also evident when a surface with a tethered polystyrene

block and a free fluorinated block had a NEXAFS spectrum almost identical to a fluorinated homopolymer surface. In other words, the polystyrene block in this case was hidden below at least the top 3 nm of the surface, the depth probed by NEXAFS. This was also confirmed by x-ray photoelectron spectroscopy measurements.

The fluorinated block copolymers we studied are unique because of their liquid crystalline properties. The fluoroalkyl side-chains of the block copolymer formed a liquid crystalline phase at the surface, with the $-(CF_2)-$ helices oriented at an angle to the surface. This orientation was quantified from the observed variation in the intensities of the peak at 292.0 eV with the angle of incidence of the x-ray beam on the surface. We found that a longer fluorinated block resulted in a higher-order parameter of



Authors Alex Hexemer (left) and Daniel Fischer

the $-(CF_2)-$ helix. The well-packed fluorinated brushes showed a remarkable stability against reconstruction of the non-polar surface when immersed in a polar environment such as water. There was only

a small decrease in the water contact angle when the surfaces were immersed in water for a week.

We propose that, in addition to their fouling-resistant properties,

surfaces bearing tethered fluorinated polymer brushes could be used to fabricate analytical devices for microbiology studies, and to create devices for the separation or microfiltration of proteins.

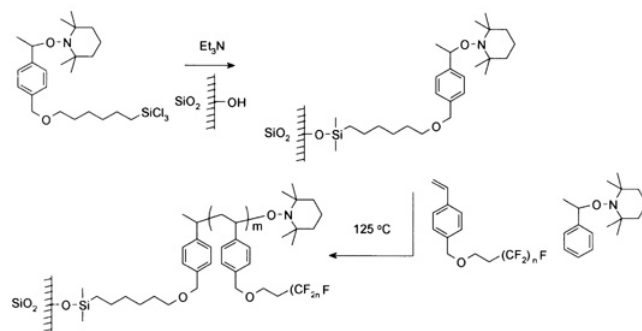


Figure 1. Synthesis of surface-grown fluorinated block copolymer brushes.

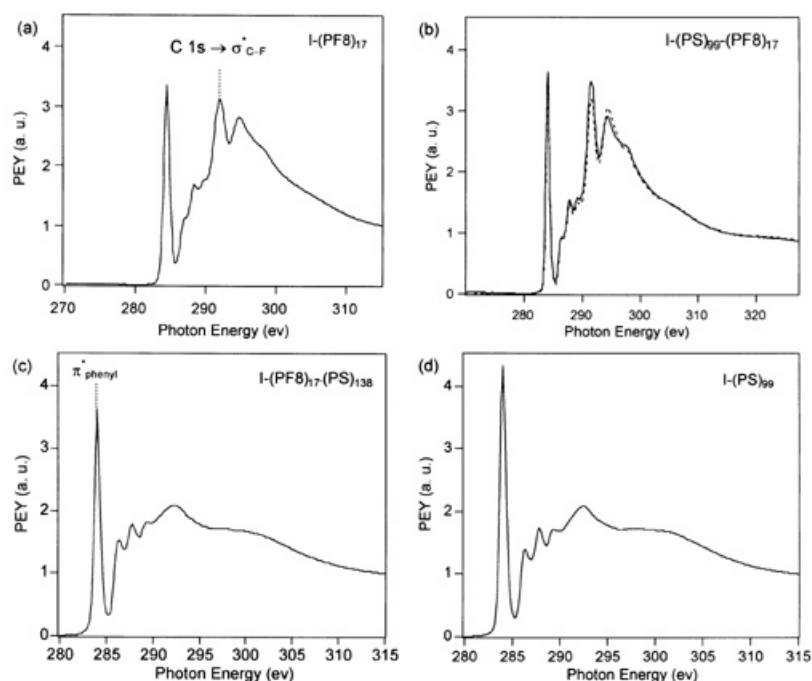


Figure 2. Carbon K-edge NEXAFS spectra of (a) fluorinated brush, (b) block copolymer brush with polystyrene block tethered to surface, (c) block copolymer brush with fluorinated block tethered to surface, and (d) polystyrene brush.